Vanadium, Chromium, and Molybdenum Contents of the Hot Springs of Japan.

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Aside from their well known mineral combinations, vanadium, chromium and molydenum have long been known to occur in a great variety of rocks. They have been detected, however, rarely in mineral waters. The occurrence of vanadium, chromium and molybdenum in a large number of Japanese mineral waters has been recently found spectroscopically by Prof. K. Kimura, and their contents in the hot springs of Yunohanazawa, Hakone, Kanagawa Prefecture have been estimated by S. Oana.[1] In the present paper the author describes the results from the quantitative estimations of these elements in a number of hot springs of Japan.

Methods of Analysis. For the determinations of vanadium, chromium and molybdenum, Sandell's colorimetric method[2] was adopted. The analytical procedures will be briefly described in the following paragraphs.

(1) *Decomposition of Sample.* 2 to 5 g. of dry residue were first fused with anhydrous sodium carbonate. The melt was leached with water and ethyl alcohol was added to reduce MnO_4^{--}. Then it was filtered. The aqueous extract contains CrO_4^{--}, VO_3^- and MoO_4^{--}, and the volume was made up to 100 c.c.

(2) *Vanadium.* A 30 c.c. portion was neutralized to methyl orange with 4N sulphuric acid and, after the addition of 8-hydroxyquinoline, vanadium was extracted by shaking with chloroform. The residue obtained by evaporating the chloroform solution was fused again with anhydrous sodium carbonate and the aqueous extract of this melt was treated with phosphotungstic acid: the yellow to orange colour was compared with that obtained with standard vanadium solutions.

(3) *Chromium.* A 10 c.c. portion was transferred to a small separting funnel, and neutralized to methyl orange with 4N sulphuric acid without using an indicator and, after the addition of 8-hydroxyquinoline, vanadium was removed by shaking with chloroform. Diphenylcarbazide and sulphuric acid were added: the red-violet colour was compared with that obtained with standard chromium solutions.

(4) *Molybdenum.* A 50 c.c. portion was transferred to a separating funnel. Concentrated hydrochloric acid, potassium thiocyanate solution and stannous chloride solution were added. The red-brown molybdenum thiocyanate was extracted with ether and the colour was compared with that obtained with standard molybdenum solutions.

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(1) Not yet published.
(2) E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **8** (1936), 336.

The Results of the Analyses. The results of the analyses are shown in Table 1.

Table 1. Vanadium Chromium and Molybdenum Contents of the Hot Springs of Japan.

Hot Springs	Parts per million of the mineral water			% (per dry residue)		
	V	Cr	Mo	V	Cr	Mo
(1) Mito, Sizuoka Prefecture	0.247	0.015	0.005	0.0190	0.0012	0.0004
(2) "Daruma-Zigoku", Yunohanazawa, Hakone, Kanagawa Prefecture	0.220	0.008	0.002	0.0105	0.0004	0.0001
(3) Monkawa, Kanagawa Prefecture	0.208	0.000	0.005	0.0007	0.0000	0.00002
(4) "Kōbō-Yu", Yunohanzawa, Hakone, Kanagawa Prefecture	0.079	0.000	0.0004	0.0079	0.0000	0.00004
(5) Matunoyama, Niigata Prefecture	0.059	0.000	0.011	0.0004	0.0000	0.00008
(6) Nanasigure, Iwate Prefecture	0.054	0.000	0.010	0.0004	0.0000	0.00008
(7) Kinkei, Totigi Prefecture .	0.051	0.073	0.002	0.0024	0.0035	0.0001
(8) "Umi-Zigoku", Beppu, Ōita Prefecture	0.022	0.003	0.001	0.0006	0.0001	0.00003
(9) Murasugi No. 3, Niigata Prefecture	0.000	0.000	0.016	0.0000	0.0000	0.0095

The hot springs of Mito had the highest vanadium content, 0.0190% (per dry residue) and the mineral waters of Murasugi No. 3 the lowest, less than 0.001% (per dry residue). The average vanadium content of nine samples was 0.005% (per dry residue). It is supposed that vanadium is associated with iron and widely distributed in the mineral waters. The mineral waters of Kinkei had the highest chromium content, 0.0035% (per dry residue). Five samples (out of nine samples) contained less than 0.0001% (per dry residue) of chromium and the author could not detect it colorimetrically. Novokhatsky and Kalinin[3] reported molybdenum to be present in a number of hot springs in the Transilian Alatau Range in quantities varying from 0.001 to 0.06% (per dry residue). It is shown in Table 1 that the small amounts of molybdenum are widely distributed in the mineral waters of Japan. The Mineral waters of Murasugi No. 3 had the highest molybdenum content, 0.0095% (per dry residue). The molybdenum content of Murasugi No. 3 was also spectroscopically estimated by the present author to be 0.01% (per dry residue), as described below.

Arc Spectrographic Detection and Estimation of Molybdenum in the Mineral Waters of Murasugi No. 3. Prof. K. Kimura found the occurrence of molybdenum in the mineral waters of Murasugi No. 3 and an arc spectrographic estimation of the element was attempted by the present author. Solutions containing 0.1, 0.01, 0.001, 0.0001 and 0.00001 mg. of molybdenum per c.c. were prepared. 10 mg. of sodium chloride was added to 1 c.c. of each solution and evaporated to dryness. Then it was placed on the lower graphite electrode and subjected to arc excita-

(3) *Compt. rend. acad. sci. U.R.S.S.*, **22** (1939), 323.

tion. The Hilger quartz spectrograph of E2 type was used. The spectral lines observed at different concentrations are described in Table 2. In this table, S signifies that the line in question is strong, W that it is weak and F that it is faintly visible.

Table 2. Spectral Lines at Different Concentrations.

λ (Å)	1 mg.	0.1 mg.	0 01 mg.	0.001 mg.	0.0001 mg.	0.00001 mg.
3041.7	W	W				
3112.1	W	W	F	F		
3132 6	S	S	W	W	F	F
3158 2	S	S	W			
3170.3	S	S	W	W	W	F
3194.0	S	S	W	F		
3208.9	S	S	W	W	W	F
3256.2	W	W				
3289.0	W	W				
3290.8	W	W				
3325.7	W	W				
3327 3	W	W				
3340.2	W					
3344.8	W	W				
3347.3	W	F				
3358.1	W	W				
3361.4	W	W				
3363 8	W	W				
3379.9	W	W				
3382.5	W	W				
3384.6	W	W	W	W	W	F
3404.4	F					
3405.9	W	W				
3418 5	F					
3447.1	W	W	F			

500 c.c. of water sample was evaporated to complete dryness. Finely powdered residue in ten milligram portions was subjected to arc excitation. The following molybdenum lines were always found.

λ (Å)	Intensity
3112.1	faint
3132.6	weak
3170.3	weak
3194.0	weak
3208.9	weak
3384.6	weak

This would seem to indicate that 0.001 mg. of molybdenum was present in the zone of excitation. Expressed in percentages,[4] the molybdenum con-

(4) Expressed in terms of parts per million of the mineral water it is supposed to be 0.02.

tent in the total residue of the mineral waters of Murasugi No. 3 is estimated to be 0.01, which is quite close to the value obtained by the colorimetric method.

Summary.

(1) The vanadium, chromium and molybdenum contents in a number of hot springs of Japan were estimated.

(2) The molybdenum content of the mineral waters of Murasugi No. 3 was spectroscopically estimated.

In conclusion, the author wishes to express his hearty thanks to Prof. K. Kimura for his kind guidance. It is also the author's pleasant duty to acknowledge the valuable advice offered by Mr. S. Oana. The expense for the experiments has been defrayed from a grant given to Prof. Kimura by The Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

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Parachor, Dipolmoment, und Molrefraktion des Selenophens.

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Die physikalischen Konstanten des Selenophens—Dichte, Brechungsindex, Dampfdruck, Ausdehnungskoeffizient, Oberflächenspannung und Parachor—wurden von Briscoe und Peel[1] angegeben, die dieses Material durch Einwirkung von Acetylen auf Selen dargestellt haben. Einer von uns (S. U.), der nach der Angaben der genannten Autoren diese Darstellungsmethode bearbeitete,[2] erhielt das Material mit guter Ausbeute. Die Darstellungsmethode lautet folgenderweise: man lässt das Acetylen auf 20 g. Selen bei 350–370°C einwirken, das sich in einem Porzellanschiffe in einem Porzellanrohr befindet. Nach der Reaktion bleibt eine schwarze, teerartige Substanz im Schiffe. Man fraktioniert das rohe Öl mittels eines Ladenburgschen Kölbchens zweimal, wobei der Hauptanteil bei 110°C übergeht und darauf erhält man aus 192 g. rohem Öl 110 g. reines Selenophen. Durch mehrmalige Destillationen erhält man eine schwach gelblich gefärbte Flüssigkeit, deren Siedepunkt 110.3–111.2°C/754.2 mm. Dichte $d_4^{25} = 1.6003$ und Brechungsindex $n_D^{25} = 1.57689$ sind. Da dieses

(1) H. V. A. Briscoe und J. B. Peel, *J. Chem. Soc.*, (London), **1928**, 1741.
(2) H. Suginome und S. Umezawa, Dieses Bulletin, **11** (1936), 157.

Präparat eine hohe Reinheit besitzen soll, was man aus den hohen Werten von Dichte und Brechungsindex ersehen kann,[3] kam es uns lohnend vor daran die physikalischen Konstanten neu zu bestimmen.

Oberflächenspannung und Parachor. Mit diesem Präparat versuchten wir zuerst die Kapillaritätskonstanten zu bestimmen. Die Oberflächenspannung wurde mittels der von einem von uns (B. T.) früher bearbeiteten Steighöhe-Methode[4] gemessen zwischen den Temperaturen von 25°C und 110°C. Der Durchmesser des gebrauchten Rohrs war bei dem engen Rohr 0,0370 cm und bei dem weiten 2 cm. Den Kontaktwinkel konnte man dadurch praktisch als null annehmen, dass man das Kapillarrohr bei jeder Messung mit Hilfe eines Magnets in die Flüssigkeit vollkommen hineintauchte. Der Messapparat befand sich in einem Wasser- bzw. Dampf-Thermostat. Die Steighöhe las man mittels eines Kathetometers mit Masstab-Ablesung von 0,005 cm ab. Die nach der Formel $\sigma=\frac{1}{2}rhg(D-d)$ berechnete Oberflächenspannung wurde nach den Tabellen korrigiert, die von Sugden[5] angegeben sind. Die Ergebnisse werden in folgender Tabelle zusammengestellt.

Tabelle 1. Spezifische Kohäsion (a^2) und Oberflächenspannung (σ) des Selenophens.

t C	h (cm.)	$D-d$	a^2 (mm.^{2})	σ (dyn./cm.)
25.0	2.476	1.6026	4.591	36.05
35 1	2.403	1.5861	4.457	34.63
56.4	2.262	1.5550	4.196	31.96
63.6	2.214	1.5420	4.107	31.02
77.5	2.100	1.5153	3.895	28.92
94.5	1.998	1.4837	3.707	26.95
110.2	1.895	1.4581	3.517	25.12

Man berechnete hierauf die Molaroberflächenenergie $\sigma\left(\frac{M}{D-d}\right)^{2/3}$ und deren Temperaturabhängigkeit (k), indem man die bekannte Katayamasche Gleichung:[6]

$$\sigma\left(\frac{M}{D-d}\right)^{2/3}=k(T_k-T)$$

anwendete. Der Mittelwert der Temperaturabhängigkeit ergab sich als 2,08 (Selenophen ist eine normale Flüssigkeit!), und unter Benutzung von diesem Wert berechnete man die kritische Temperatur, die sich im Mittelwert als 624.3°K ergab. Ferner bestimmte man das Parachor

(3) Vgl. mit Briscoe und Peelschen Daten: $d_4^{15}=1.5301$ und $n_D^{15}=1.568$.
(4) B. Tamamushi, Dieses Bulletin, **1** (1926), 173.
(5) S. Sugden, *J. Chem. Soc.*, (London) **1921**, 1483.
(6) M. Katayama, *Sci. Rep. Tohoku Imp. Univ.*, **4** (1915), 373.

$P = \frac{M}{D-d}\sigma^{\frac{1}{4}}$. Die Ergebnisse sind in Tabelle 2 gezeigt. Die hierbei verwendeten Dampfdichten wurden mittels der von Briscoe und Peel[1] angegebenen Daten von Dampfdruck berechnet.

Tabelle 2. Molaroberflächenenergie $\left(\sigma\left(\frac{M}{D-d}\right)^{2/3}\right)$, Temperaturkoeffizient (k), Parachor (P), und kritische Temperatur (T_k).

t°K	$\sigma\left(\frac{M}{D-d}\right)^{2/3}$	k	P	T_k^cK
298.0	679.1		200.3	624.7
		2.20		
308.1	656.9		200.4	623.9
		2.00		
329.4	614.3		200.4	624.2
		2.04		
336.6	599.6		200.5	625.3
		2.44		
350.5	565.6		200.5	622.4
		1.83		
367.5	534.4		201.2	624.3
		1.94		
383.2	504.0		201.2	625.5
		(2.08)	(200.6)	(624.3)

Aus den grösseren Werten von Oberflächenspannung und Dichte folgt der kleinere Wert von Parachor im Vergleich mit den Briscoe und Peelschen Resultaten. Berechnet man aus diesen Werten von Parachor den Wert von Atomparachor des Selens, so bekommt man bei uns 58,3, während man dafür 68,0 bei Briscoe und Peel erhält, wobei man die folgenden Atom- bzw. Gruppen-Parachore verwendet.

C = 4.8 H = 17.1 = 23.2 = 8.5

Unter Benutzung der Messungsdaten an den fünf organischen Selen-Verbindungen (Diphenyl-Selenid usw.) hat zwar Sugden[7] für das Atomparachor des Selens den Wert 62.5 (im Mittelwert) angenommen, woraus man das Parachor des Selenophens berechnet und dabei 205.0 erhält. Dieser Wert liegt gerade zwischen dem von uns beobachteten Wert und dem von Briscoe und Peel beobachteten (210.6): die Übereinstimmung zwischen den berechneten und beobachteten ist jedoch bei uns näher, und zwar tritt bei uns eine Depression des Parachors hervor, dagegen eine Exaltation bei Briscoe und Peel. Es scheint noch fraglich, ob man zwischen der Depression des Parachors und dem aromatischen Charakter des Selenophenringes auf einen Zusammenhang schliessen kann, denn eine solche Depression lässt sich in anderen aromatischen Verbindungen noch nicht allgemeingültig erkennen.

Dipolmoment. Das Dipolmoment wurde durch die Messung der Dielektrizitätskonstante und Dichte der binären Flüssigkeitsgemische bestimmt, indem man für die dipolfreie Flüssigkeit einmal Benzol und

(7) S. Sugden, "The Parachor and Valency," S. 126 London (1930).

ein anderesmal Hexan verwendete. Die beiden Lösungsmittel waren sorgfältig gereinigte Präparate. Der für die Dielektrizitätskonstante (DK)-Messung gebrauchte Apparat war der elektrische Schwebungsapparat, dessen Sender auf einer Grundschwingung von 200 m arbeitete. Die Kapazität des Präzisionskondensators war 150 mmf. mit Feinregulierung von 0,06 mmf. Den Messkondensator baute man nach Estermann[8], indem man ein Platinblech in einem Glasrohr anlötete, und stellte ihn in einen Paraffin-Thermostat. Die ganze Apparatur war durch geerdelte Metallumhüllung geschützt, durch welche nur das Führrohr des Messkondensators, die Feineinstellung der veränderlichen Kapazität und die Leitung des Telephons geführt waren.

Die Apparatur wurde empirisch geeicht und zwar zunächst mit Hilfe der verdünnten Lösungen von Äthyläther in Benzol: die Ergebnisse sind in fogender Tabelle angegeben, wobei man als DK des Benzols den von Williams[9] angegebenen Wert 2.282 (später unten 2.276) bei 25°C anwendete.

Tabelle 3. Molekulare Polarisation des Äthyläthers.
In Benzol bei Temp. 25°C.

f_2 (%)	d_4^{25}	ε	$P_{1,2}$	P_2
0	0.8733	2.282	26.77	56.7
25	0.8312	2.752	34.11	56.4
50	0.7907	3.225	41.00	55.2
75	0.7494	3.809	48.45	55.7
100	0.7089	4.330	54.96	55.0

Die Kolonnen der Tabelle bedeuten von links nach rechts: f_2 den Molenbruch des gelösten Stoffes, d_4^{25} die Dichte der Lösung, ε die gemessene DK, $P_{1,2} = \frac{\varepsilon-1}{\varepsilon+2} \cdot \frac{f_1M_1+f_2M_2}{d}$ die Molekularpolarisation der Lösung und $P_2 = \frac{P_{1,2}-f_1P_1}{f_2}$ die Molekularpolarisation des gelösten Stoffes.

Man kann mit Hilfe von der bekannten Debyeschen Grundformel aus der Molekularpolarisation P_2 das elektrische Dipolmoment des gelösten Stoffes folgendermassen berechnen. Die Molekularpolarisation besteht aus zwei Teilen, nämlich der Polarisation infolge Ladungsverschiebungen P_2'' und der Polarisation infolge der Orientierung festiger Dipole $P_2' = \frac{4\pi}{3} N \frac{\mu^2}{3kT}$ und demnach bekommen wir $P_2' = P_2 - P_2''$.

P_2'' wird nun annähernd berechnet nach der Lorenz-Lorentzschen Formel: $P_2'' = \frac{n_0^2-1}{n_0^2+2} \cdot \frac{M}{d}$, wobei n_0 den Brechungsindex des gelösten Stoffes, extrapoliert für die Frequenz 0, bedeutet. Diese Extrapolation

(8) J. Estermann, *Ergeb. Exakt. Wiss.*, **8** (1929), 279.
(9) J. W. Williams, *Physik. Z.*, **29** (1928), 174; ebenda **32** (1931), 27.

kann zwar nur ausgeführt werden, wenn die Substanz keine ultraroten Absorptionen zeigt. Wenn dieses Vorgehen infolgedessen auch nicht als ganz exakt angesehen werden darf, so ergibt es doch manchmal einen genügend genauen Wert für den Teil P_2''. Der Einfachheit wegen nehmen wir noch für P_2', $\frac{n_D^2-1}{n_D^2+2}\cdot\frac{M}{d}$ statt $\frac{n_0^2-1}{n_0^2+2}\cdot\frac{M}{d}$, was auch manchmal der Fall ist.

Für den Fall von Äthyläther fanden wir $P_2'' = 22{,}5$, woraus sich das Dipolmoment folgenderweise ausrechnen liess:

$$P_2' = P_2 - P_2'' = 55.8 - 22.5 = 33.3\ \text{cm.}^3$$

$$P_2' = \frac{4\pi}{3} N \frac{\mu^2}{3kT} = 33.3\ \text{cm.}^3$$

$$\mu = 1.26 \cdot 10^{-18}\ \text{e. s. E.}$$

Tabelle 4 und 5 zeigen die Ergebnisse der Messung der Molekularpolarisation mit Selenophen. Man ermittelt hieraus nach der oben geschilderten Methode das elektrische Momement des Selenophens einmal in Benzol-Lösungen mit dem Ergebnis: $\mu = 0.78 \cdot 10^{-18}$, und ein andersmal in Hexan-Lösungen mit dem Ergebnis: $\mu = 0.77 \cdot 10^{-18}$.

Tabelle 4. Molekulare Polarisation des Selenophens.
In Benzol bei Temp. 25°C.

f_2 (%)	d_4^{25}	ε	$P_{1,2}$	P_2
0.000	0.8731	2.276	26.68	(39.9)
2.684	0.8908	2.305	27.05	40.6
4.058	0.8997	2.314	27.17	38.7
5.578	0.9101	2.324	27.27	37.1
7.427	0.9226	2.344	27.50	37.8
10.260	0.9424	2.370	27.77	37.3
24.670	1.0419	2.422	28.13	32.6

$P_2'' = 27.1$ $\quad P_2' = 12.8$ $\quad \mu = 0.78_1 \cdot 10^{-18}$

Tabelle 5. Molekulare Polarisation des Selenophens.
In Hexan bei Temp. 25°C.

f_2 (%)	d_4^{25}	ε	$P_{1,2}$	P_2
0.000	0.6691	1.880	29.19	(39.6)
3.997	0.6924	1.908	29.50	36.8
7.324	0.7069	1.917	29.67	35.6
9.198	0.7246	1.936	29.62	33.8

$P_2'' = 27.1$ $\quad P_2' = 12.5$ $\quad \mu = 0.77_2 \cdot 10^{-18}$

Zum Vergleich tragen wir das oben bestimmte Dipolmoment des Selenophens mit den Dipolmomenten von Furan und Thiophen in die folgende Tabelle ein, woraus man sieht, dass das Dipolmoment des Selenophens etwas grösser als diejenigen von Furan oder Thiophen ist. Solange man aber die Bestimmungsmethode, die auf eine Vernachlässigung von Atompolarisation hinausläuft, anwendet, kann man einen Fehler kaum umgehen. Zur Bestimmung des genaueren Dipolmoments des Selenophens wäre es wünschenswert, wie Kubo[14] mit Thiophen getan hat, die Messung im Dampfzustand auszuführen.

Tabelle 6. Dipolmoment heterocyclischer Verbindungen.

Substanz	Dipolmoment (i. Debye E.)	Autor
Furan	0.63 (Benzol)	Partington[10]
	0.71 (Benzol)	Smyth[11]
Thiophen	0.63 (Benzol)	Hassel[12]
	0.54 (Hexan)	Higashi[13]
	0.58 (Dampf)	Kubo[14]
Selenophen	0.78 (Benzol)	Tamamushi, Akiyama, und Umezawa
	0.77 (Hexan)	

Unter Annahme, dass im Ringe zwei Doppelbindungen existieren und dass man für den Valenzwinkel des Kohlenstoffes 125°C einsetzen kann, hat Smyth und Walls[11] den Valenzwinkel des Sauerstoffes bzw. des Schwefels auf mehr als 140°C abgeschätzt, der mit den kleinen Dipolmomenten dieser Stoffe entspricht. Unter der gleichen Annahme ergibt sich der Valenzwinkel des Selens aus dem beobachteten Dipolmoment als etwa 140°C (kleiner als bei Furan und Thiophen!), indem man für das Gruppenmoment C-Se = 1.1 anwendet.[15] Diese Betrachtungen sind aber nicht am Platz, denn die Feststellung, dass sowohl Furan oder Thiophen als auch Selenophen die gewöhnlichen Doppelbindungen enthalten, ist nach unseren heutigen Kenntnissen sehr unwahrscheinlich. Diese Sachlage wird noch aus der Depression in Molrefraktion dieser Stoffe wahrgenommen, worüber unten berichtet werden soll.

Molrefraktion. Die Molrefraktion des Selenophens wurde bei 25°C bestimmt, indem man den Brechungsindex mittels einem Pulfrichschen Refraktometer mass: die Ergebnisse werden in Tabelle 7 angegeben.

Ermittelt man aus der erhaltenen Molrefraktion (MR_D) die Atomrefraktion des Selens, wobei man die Eisenrohrschen Atom- bzw. Gruppen-Refraktionen, nämlich: C = 2.418, H = 1.100, F = 1.733 anwendet, so

(10) J. Partington und E. C. E. Hunter, *J. Chem. Soc.*, London, **1931**, 2062.
(11) C. P. Smyth und W. S. Walls, *J. Amer. Chem. Soc.*, **54** (1932), 3230.
(12) O. Hassel und E. Naeshagen, *Chem. Zentr.*, **1930**, 1956.
(13) K. Higashi, *Bull. Inst. Phys. Chem. Res.*, (Tokyo) **11** (1932), 729.
(14) M. Kubo, *Sci. Pap. Inst. Phys. Chem. Res.*, (Tokyo) **29** (1936), 122.
(15) Gruppenmoment: C-Se = 1.08, C-O = 0.94, C-S = 1.16. Siehe N. V. Sidgwick, "The Covalent Link in Chemistry," S. 150, New York (1933).

Tabelle 7. Molrefraktion des Selenophens bei 25°C.

	n_D^{25}	MR_D
C	1.57082	26.90
D	1.57689	27.12
F	1.59218	27.71
G′	1.60578	28.22

ergibt sich die Atomrefraktion: Se = 9.59. Dieser Wert der Atomrefraktion ist bedeutend kleiner als die Werte (10–11), die man für die Atomrefraktion des Selens aus den Daten von aliphatischen Seleniden oder von gesättigten cyclischen Selenverbindungen gefunden hat.[16] Dies deutet darauf hin, dass im Selenophen eine bedeutende Depression der Molrefraktion stattfindet. Diese Depression wird z. B. folgenderweise berechnet. Nach den von Morgan und Burstall[17] gewonnenen Daten (n_D^{18} = 1·5510, d_4^{18} = 1.4816) an Tetrahydroselenophen (eine gesättigte Verbindung des Selenophens), setzt man für die Molrefraktion dieses Stoffes MR_D = 29.08, woraus man für die Atomrefraktion des Selens Se = 10.61 erhält. Berechnet man nun die Molrefraktion des Selenophens unter Benutzung der hier erhaltenen Atomrefraktion, so bekommt man 28.15, und demnach für die molekulare Exaltation EM_D = –1.03 und für die spezifische Exaltation $E\Sigma_D$ = –0.79.

Das Selenophen verhält sich also ähnlich wie andere heterocyclischen Verbindungen (Furan, Pyrrol, und Thiophen) oder Benzol, wobei auch die Depression in Molrefraktion mehr oder weniger zutage kommt. Die Tabelle 8 gibt die molekulare- bzw. spezifische Exaltation dieser heterocyclischen Verbindungen wieder.[18]

Tabelle 8. Molekulare- und spezifische Exaltation cyclischer Verbindungen.

Substanz	EM_D	$E\Sigma_D$
Benzol	−0.17	−0.22
Furan	−0.75	−1.10
Pyrrol	−0.22	−0.33
Thiophen	−1.08	−1.31
Selenophen	−1.03	−0.79

(16) Atomrefraktion des Selens: z.B. 10.48 (aus Dimethylselenid) Y. Tanaka und Y. Nagai, *J. Soc. Chem. Ind.*, (Japan), **30** (1927), 171 B. 10.94 (aus Diäthylselenid) J. Zoppellari, *Gazz. Chim. Ital.*, **24**, II, 396. 10.85 (aus Methyläthylselenid) L. Tschgaeff, *Ber.*, **42** (1909), 49. 10.22 (aus Cycloselenohexan), 10.66 (aus Cycloselenopentan), 10.61 (aus Tetrahydroselenophen) G. T. Morgen und F. H. Burstall, *J. Chem. Soc.*, (London), **1929**, 2197, ebenda **1931**, 173.

(17) G. T. Morgan und F. H. Burstall, *J. Chem. Soc.*, (London), **1929**, 2197.

(18) Zusammengestellt von v. Auwers, *Lieb. Ann.*, **408** (1915), 257 f.

Die Ursache dieser Depression in Molrefraktion dürfte man darin suchen, wie W. Hückel in seinem Lehrbuch angedeutet hat,[19] dass bei diesen cyclischen Verbindungen die Einflüsse endocyclischer Konjugation und der Störungen ganz anderer Art als bei acyclischen sind. Die Betrachtung, dass das Selenophen wie Thiophen oder Furan im allgemeinen einen aromatischen Charakter besitzen soll, steht mit unseren Erfahrungen die chemischen Eigenschaften dieses Soffes betreffend im Einklang.[20] Das Selenophen verhält sich in der Tat sehr ähnlich wie Thiophen in der chemischen Reaktionsweise, obgleich das erstere zuweilen einen mehr ungesättigten Charakter als das zweite aufweist, indem das zweiwertige Selen zum vierwertigen übergeht.

Der aromatische Charakter des Pyrrols, Furans, und Thiophens, worin man eine quantenmechanische Resonanz zwischen zwei Formen annehmen kann, wurde von Bonino[21] in seinen Untersuchungen der Ramanspektren von diesen Stoffen konstatiert. Es wäre interessant das Ramanspektrum auch mit Selenophen zu untersuchen, was wir noch in Zukunft vornehmen möchten.

Zusammenfassung.

An dem Selenophen-Präparat mit hoher Reinheit wurden die physikalischen Konstanten: Dichte $d_4^{25} = 1.6003$, Brechungsindex $n_D^{25} = 1.57689$, Molrefraktion $MR_D = 27.12$, Oberflächenspannung $\sigma^{25} = 36.05$ dyn./cm., Temperaturabhängigkeit der Molaroberflächenenergie $k = 2.08$, Parachor $P = 200.6$ und elektrisches Dipolmoment $\mu = 0.78 \cdot 10^{-18}$ (in Benzol), $\mu = 0.77 \cdot 10^{-18}$ (in Hexan) bestimmt.

Auf Grund dieser Daten wurde eine Diskussion über die Struktur dieses Stoffes dargelegt, insbesondere in Bezug auf den aromatischen Charakter dieses Stoffes.

Nedzu Chemisches Laboratorium der Musashi Hochschule, Tokyo und Chemisches Institut der Kaiserlichen Hokkaido Universität, Sapporo.

(19) W. Hückel, "Theoretische Grundlagen der organischen Chemie," II, S. 99, Leipzig (1931).

(20) S. Umezawa, Dieses Bulletin, **11** (1936), 157; **11** (1936), 775; **12** (1937), 4; **14** (1939), 155. W. Steinkopf, *Lieb. Ann.*, **532** (1937), 253.

(21) G. B. Bonino, R. Manzoni-Ansidei, und P. Pratesi, *Z. physik. Chem.* B, **22** (1933), 21; ebenda **25** (1934), 327.

Dipolmoment und Struktur der isomeren Selenophthene.

Von Bun-ichi TAMAMUSHI, Hajime AKIYAMA und Sumio UMEZAWA.

(Eingegangen am 25. Juli 1939.)

In den synthetischen Untersuchungen in der Selenophengruppe gelang es einem von uns (S. U.) drei isomere Selenophthene $C_6H_4Se_2$ rein zu gewinnen, die folgenderweise entstanden sind.

Destilliert man das durch die Einwirkung von Acetylen auf Selen entstandene schwarzbraune Oel, so gewinnt man Selenophen im Destillat, während sich aus dem Rückstand nach langer Zeit (über einen Monat) eine Substanz auskristallisiert, die aus Alkohol rekristallisiert wird. Diese Substanz, eine Form der Selenophthene, mit dem Schmelzpunkt 123–124.5° wird im folgenden mit dem Buchstaben (B) gekennzeichnet.

Das Filtrat teilt man durch Wasserdampfdestillation in zwei Teile, ein Pikrat-bildender Anteil und ein anderer Pikrat-nichtbildender. Der erste Anteil wird durch Ammoniak zersetzt und dann wird das dadurch wiedergewonnene Oel unter Vakuum destilliert. Nach wiederholter Rekristallisation mit Pikrat und Vakuumdestillation erhält man eine kristalline Substanz, die aus Alkohol rekristallisiert wird. Die Ausbeute ist zwar sehr gering. Diese Substanz, eine andere Form der Selenophthene, mit dem Schmelzpunkt 51–51.5° wird mit dem Buchstaben (A) bezeichnet.

Der Pikrat-nichtbildende Anteil wird nach mehrmaligen Wasserdampfdestillationen unter Vakuum destilliert, wobei man ein Oel von dem Siedepunkt 93°/14 mm. gewinnt. Diese Substanz, eine dritte Form der Selenophthene, wird im folgenden mit (C) gekennzeichnet.

Die Eigenschaften dieser drei Isomeren und ihrer Derivate sind in Tabelle 1 zusammengestellt.

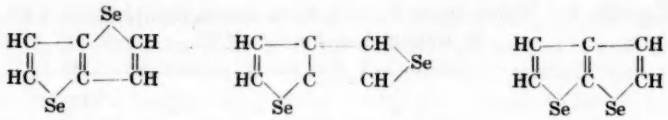
Tabelle 1. Konstanten der isomeren Selenophthene und ihrer Derivate.

Selenophthen	Pikrat	Tetrabrom-Selenophthen
(A) Schmp. 51–51.5°	Schmp. 154–155.5°	Schmp. 252.5–253° (korr.)
(B) Schmp. 123–124.5°	Schmp. 163–165°	Schmp. 246–247.5° (korr.)
(C) Sdp. 90–93°/14 mm.	—	Schmp. 271–272° (korr.)

In Anbetracht der Challenger und Harrisonschen Untersuchungen[2] über die isomeren Thiophthene, könnte man nun für die oben isolierten Selenophthen–Isomeren folgende möglichen Strukturen aufstellen:

(1) S. Umezawa, Dieses Bulletin, **11** (1936), 197; **11** (1936), 775; **12** (1937), 4; **14** (1939), 155.

(2) F. Challenger und J. B. Harrison, *J. Inst. Petroleum Technologists*, **21** (1935), 135.



I II III

Es ist unsere Aufgabe zu bestimmen, welche von diesen Strukturen je einem von den oben erhaltenen drei Isomeren entspricht. Zu diesem Zweck haben wir die Methode der Dipolmoment-Bestimmung angewandt, die sich tatsächlich als zweckdienlich erwies.

Die Methode der Bestimmung des elektrischen Dipolmoments war dieselbe, die in der vorangehenden Arbeit[3] beschrieben worden ist. Die DK-Messungsapparatur arbeitete bei Frequenz von 200 m und die Messungen wurden bei 25°C und zwar in binären Gemischen in Benzol ausgeführt. Die Ergebnisse sind in Tabellen 2–4 angegeben, wobei f_2 den Molenbruch des gelösten Stoffes, d_4^{25} die Dichte der Lösung, ε die Dielektrizitätskonstante, $P_{1,2}$ die Molekularpolarisation der Lösung, P_2 die Molekularpolarisation des gelösten Stoffes, $MR_{1,2}$ die Molrefraktion der Lösung und MR_2 die Molrefraktion des gelösten Stoffes bedeutet.

Tabelle 2. Molekulare Polarisation des Selenophthens (C). In Benzol bei Temp. 25°C.

f_2 (%)	d_4^{25}	ε	$P_{1,2}$	P_2
0.000	0.8731	2.276	26.71	(92.6)
1.070	0.8896	2.316	27.35	86.9
2.039	0.9033	2.337	27.76	79.4
3.374	0.9221	2.367	28.30	73.8

$P_2''(MR_D) = 44.6$ $P_2' = 48.0$ $\mu = 1.52 \cdot 10^{-18}$

Tabelle 3. Molekulare Polarisation des Selenophthens (B). In Benzol bei Temp. 25°C.

f_2 (%)	d_4^{25}	ε	$P_{1,2}$	P_2	n_D^{25}	$MR_{1,2}$	MR_2
0.000	0.8731	2.276	26.71	(75)	1.49664	26.17	(51)
0.680	0.8841	2.295	27.00	70.5	1.49912	26.29	45.5
0.879	0.8861	2.299	27.13	76.2	1.50004	26.40	52.3
1.074	0.8882	2 306	27.27	76.3	1.50054	26.46	54.0
1.308	0.8930	2.309	27.27	71.1	1.50117	26.46	48.2
2.172	0.9062	2.327	27.60	67.7	1.50490	26.69	50.2

$P_2''(MR_D) = 51$ $P_2' = 24$ $\mu = 1.07 \cdot 10^{-18}$

(3) Dieses Bulletin, Diese Heft, S. 310.

Tabelle 4. Molekulare Polarisation des Selenophthens (A).
In Benzol bei Temp. 25°C.

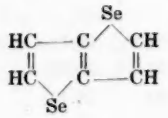
f_2(%)	d_1^{25}	ε	$P_{1,2}$	P_2	n_D^{25}	$MR_{1,2}$	MR_2
0.000	0.8731	2.276	26.71	(52)	1.49664	26.17	(56)
0.811	0.8855	2.282	26.85	43	1.50172	26.43	59
1.589	0.8950	2.292	27.11	52	1.50415	26.67	59
2.479	0.9131	2.329	27.58	62	1.50684	26.73	49

$$P_2''(MR_D) = 56 \qquad P_2' \cong 0 \qquad \mu \cong 0$$

Die Bestimmung der Molrefraktion wurde bei dem flüssigen Selenophthen (C) an der reinen Flüssigkeit durchgeführt mit dem Ergebnis: $n_D^{25} = 1.6586$, $d_4^{25} = 1.9354$ und demnach $MH_D = 44.6$, während sie bei den festen Präparaten (A) und (B) in benzoligen Lösungen ausgeführt wurde: die erhaltenen Daten sind in Kolonnen 6, 7, 8 in Tabelle 3 und 4 angegeben. In den letzten zwei Fällen liefert Extrapolation für die Konzentration null die Molrefraktion des gelösten Stoffes. Infolge der sehr geringen Ausbeute des erhaltenen Präparates bei den festen Isomeren, besonders bei der Form (A), war es schwierig die DK-Messungen sowie Brechungsindex-Messungen mit genügender Genauigkeit durchzuführen, man konnte sogar nicht die Messung wiederholen. Mit dem Präparat (B) konnte man indessen sowohl P_2 als auch MR_2 durch Extrapolation feststellen, während man mit dem Präparat (A) den Wert von P_2 sowie MR_2 nur als Mittelwert annähernd abschätzen konnte, indem man als Mittelwert sowohl von P_2 als auch von MR_2 einen gleichen Wert, etwa 50, aufnahm.

Wir stellten in dieser Weise das Dipolmoment folgendermassen fest: für den flüssigen Isomer (C) $\mu = 1.52 \cdot 10^{-18}$, für den einen festen Isomer (B) $\mu = 1.07 \cdot 10^{-18}$ und für den andern festen Isomer (A) $\mu \cong 0$.

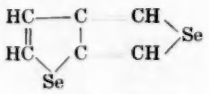
Wir nehmen nun an, dass ein Selenophthen-Molekül durch Kondensation von zwei regulär pentagonalen Selenophen-Ringen aufgebaut ist. Berechnet man unter dieser Annahme das elektrische Moment des Selenophthen-Moleküls, wobei man das in der vorangehenden Arbeit[3] festgestellte Gruppenmoment des Selenophen-Ringes benutzt, so erhält man folgende Dipolmomente je nach der Strukturformel (I), (II) und (III).



I

$\mu_{ber.} = 0$

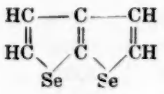
$\mu_{beo.} = 0$



II

$\mu_{ber.} = 0.92 \cdot 10^{-18}$

$\mu_{beo.} = 1.07 \cdot 10^{-18}$



III

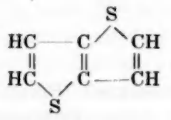
$\mu_{ber.} = 1.48 \cdot 10^{-18}$

$\mu_{beo.} = 1.52 \cdot 10^{-18}$

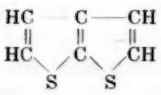
Hiernach findet man eine deutliche Uebereinstimmung zwischen den beobachteten und den berechneten Dipolmomenten. Es folgt nämlich, dass

der erste Isomer(A) der Struktur (I) d. h. eine trans-Form, der zweite Isomer(B) der Struktur (II) d. h. eine andere trans-Form und der dritte Isomer (C) der Struktur (III) d. h. eine cis-Form entspricht.

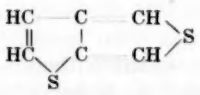
Zur Strukturbestimmung der isomeren Thiophthene haben auch Challenger und Harrison[2] die Methode der Dipolmoment-Messung in Betracht gezogen. Von drei Thiophthen-Isomeren wurden dabei einer im festen Zustand und die anderen im flüssigen, gewonnen. Das Dipolmoment des ersten war gleich null (Messung von Goss) gefunden, wodurch dieser der Struktur (I) entspricht, während die Dipolmomente der anderen flüssigen Isomeren gleich $1.16 \cdot 10^{-18}$ bzw. $1.03 \cdot 10^{-18}$ waren, welche demnach der Struktur (II) oder (III) zuzuordnen sind. Es scheint aber, dass die beiden flüssigen Verbindungen damals noch nicht ganz rein getrennt waren.



I



II



III

Bemerkenswert sind die analogen Beziehungen in den Thiophthen–Isomeren und in den Selenophthen-Isomeren. Es gibt indessen bei Selenophthen zwei feste (trans) und eine flüssige (cis) Verbindung, während bei Thiophthen eine feste (trans) und zwei flüssige (cis und trans) Verbindungen existieren. Die Schlussfolgerung aus Dipolmoment-Bestimmung über die Struktur dieser Verbindungen scheinen in den beiden Fällen schon sehr bedeutsam. Zur Struktur-Feststellung dieser Isomeren wäre es immerhin wünschenswert, weitere Kenntnisse zu erwerben sowohl bei Thiophthen als auch bei Selenophthen.[4] Die chemische Untersuchung in bezug auf die Selenophthene wird von einem von uns (S. U.) noch an anderer Stelle berichtet werden.

Die Molrefraktion des oben gewonnenen flüssigen Selenophthens (C) ist nach den Daten $n_D^{25} = 1.6586$, $d_4^{25} = 1.9354$ gleich 44.55 gesetzt. Die unter Anwendung von Atomrefraktion des Selens Se = 10.61 (ermittelt aus der Molrefraktion des Tetrahydroselenophens[5]) berechnete Molrefraktion des Selenophthens ist anderseits gleich 45.33. Demnach ist die molekulare Exaltation $EM_D = -0.78$ und die spezifische Exaltation $E\Sigma_D = -0.33$. Es kommt also hier eine Depression hervor.

Bekanntlich zeigt Naphthalin eine deutliche Exaltation,[6] nämlich $EM_D = 2.28$, während Thionaphthen eine kleinere Exaltation $EM_D = 0.93$ aufweist, was wahrscheinlich darauf beruht, dass der Einfluss der Exaltation in kondensierten Ringen durch den Einfluss der Depression im Thiophenring kompensiert wird. Bei Selenophthen, wo eher eine Depres-

(4) Bei Thiophthenen sind auch die Kenntnisse röntgenographischer Analyse an dem festen Isomer zur Struktur-Bestimmung benutzt worden (Challenger und Harrison).

(5) G. T. Morgan und F. H. Burstall, *J. Chem. Soc.*, (London), **1929**, 2197. Vgl. unsere vorangehende Arbeit, Diese Heft, S. 317.

(6) R. Kremann, "Physikalische Eigenschaften und chemische Konstitution," S. 78, Dresden (1937).

sion stattfindet, müssten die Einflüsse der Depression in den Selenophenringen superponiert stark zur Wirkung gelangen. Tabelle 5 gibt die molekulare- bzw. spezifische Exaltation der oben erwähnten kondensierten Ringverbindungen wieder.

Tabelle 5. Molekulare- und spezifische Exaltation von Naphthalin, Thionaphthen und Selenophthen.

Substanz	EM_D	$E\Sigma_D$
Naphthalin	+2.28	+1.78
Thionaphthen	+0.93	+0.69
Selenophthen (cis)	−0.78	− 0.33

Das Selenophthen stellt jedenfalls ein interessantes Beispiel der kondensierten Ringverbindungen dar, in welchem eine Depression in Molrefraktion zur Erscheinung kommt.

Zusammenfassung.

Die Struktur der drei rein isolierten Isomeren des Selenophthens wurde mit Hilfe der Dipolmoment-Bestimmung festgestellt. Ein fester Isomer (Schmp. 51–51.5°) mit dem Dipolmoment $\mu = 0$ entspricht der trans-Form, ein anderer fester Isomer (Schmp. 123–124.5°) mit dem Dipolmoment $\mu = 1.07 \cdot 10^{-18}$ der anderen trans-Form und ein flüssiger Isomer mit dem Dipolmoment $\mu = 1.52 \cdot 10^{-18}$ der cis-Form.

Es wurde auf die Depression in Molrefraktion des flüssigen Selenophthens aufmerksam gemacht.

Nedzu Chemisches Laboratorium der Musashi Hochschule, Tokyo und Chemisches Institut der Kaiserlichen Hokkaido Universität, Sapporo.

The Mechanism of the Oxygen Effect on Hydrogen Bromide Reacting with Ethenoid Compounds.

By Yoshiyuki URUSHIBARA and Osamu SIMAMURA.

(Received July 28, 1939.)

Introduction.[1] In 1933, at the Dyson Perrins Laboratory, Oxford, one (Y.U.) of the authors had occasion to prepare 11-bromoundecanoic acid by adding hydrogen bromide to undecenoic acid according to the work by Walker and Lumsden.[2] Undecenoic acid was dissolved in toluene, a portion of toluene was distilled off to remove moisture, and hydrogen bromide was passed immediately into the cooled solution, when 10-bromoundecanoic acid was found to be the main product. On the other hand, when undecenoic acid was dissolved in toluene, both after being dried separately, and without distillation of the solvent hydrogen bromide was passed into the solution, the product was 11-bromoundecanoic acid. At that time it was assumed that the difference was caused by traces of moisture entering when the solution was prepared.[3]

Kharasch and Mayo[4] soon found that hydrogen bromide adds to pure allyl bromide in the absence of oxygen to give mainly 1,2-dibromopropane (normal reaction) while in the presence of peroxides or oxygen 1,3-dibromopropane is the main product (abnormal reaction). The effect was attributed to the action of peroxides and called "peroxide effect." The effect can be eliminated by the addition of antioxidants, e.g. diphenylamine and hydroquinone. Later Urushibara and Takebayashi[5][6] showed that the effect of oxygen is caused by the action of molecular oxygen and suggested the possibility that the effect of peroxides might be due to the action of molecular oxygen generated by the decomposition of the peroxides. Further it was demonstrated that the abnormal reaction caused by oxygen is homogeneous.[7]

Ashton and Smith[8] studied the addition of hydrogen bromide to undecenoic acid in the light of Kharasch's observations and found that oxygen is the agent reversing the direction of addition also in this case.

Urushibara and Takebayashi,[9] studying the effects of various substances other than oxygen and peroxides, observed that ferromagnetic metals such as reduced nickel and reduced iron influence the addition of hydrogen bromide to allyl bromide quite in the same way as oxygen. Reduced nickel was found effective also in reversing the direction of

(1) Compare J. C. Smith, *Chemistry and Industry*, **56** (1937), 833; **57** (1938), 461.
(2) J. Walker and J. S. Lumsden, *J. Chem. Soc.*, **79** (1901), 1191.
(3) Compare *Chemistry and Industry*, **52** (1933), 219.
(4) M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55** (1933), 2468.
(5) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 798.
(6) *Idem, ibid.*, **12** (1937), 138.
(7) *Idem, ibid.*, **12** (1937), 173.
(8) R. Ashton and J. C. Smith, *J. Chem. Soc.*, **1934**, 435.
(9) Y. Urushibara and M. Takebayashi, this Bulletin, **11** (1936), 692, 754; **12** (1937), 51; **13** (1938), 400.

addition of hydrogen bromide to undecenoic acid in toluene solution.[10] While diphenylamine hardly affects the influence of reduced nickel and reduced iron, hydroquinone and catechol inhibit the action of reduced nickel to a great extent.[12][13] Reduced nickel and reduced iron are stable to hydrogen bromide under the conditions of the experiments, while reduced cobalt is so liable to attack by hydrogen bromide that the effect of the metal is only moderately displayed.[11][14]

The peculiar influence of oxygen and the ferromagnetic catalysts on hydrogen bromide has been observed further in the isomerization of isostilbene to stilbene, a reaction apparently quite different from the addition reactions. Kharasch and co-workers[15] found that in the dark pure isostilbene, dissolved in benzene, is not isomerized to stilbene by hydrogen bromide alone, but the addition of a peroxide to the mixture causes complete isomerization in a few minutes. The present authors[16][17] extended Kharasch's observation to oxygen and to the ferromagnetic catalysts, viz., reduced nickel and reduced iron. Isostilbene, in the pure liquid state or in benzene solution, is isomerized to stilbene by hydrogen bromide in the presence of oxygen in the dark at room temperature. Reduced nickel and reduced iron also co-operate with hydrogen bromide to isomerize isostilbene, although the effect of hydrogen bromide in the presence of the ferromagnetic catalysts is much smaller than in the presence of oxygen under the conditions of the experiments. The strengths of the inhibiting actions of diphenylamine and catechol on oxygen and reduced nickel are quite parallel to those displayed in the cases of the addition reactions.[17]

A theory on the mechanism of the effect of oxygen or peroxides as outlined above have been presented by Kharasch and co-workers.[15][18] The cis-trans isomerization caused by bromine and light is attributed to the action of bromine atoms.[19] Isostilbene is isomerized by hydrogen bromide not only in the presence of peroxides but also in sunlight, and hydroquinone inhibits the isomerization in either case.[15] Further the transformation of ethyl α-bromoacetoacetate into ethyl γ-bromoacetoacetate by hydrogen bromide is accelerated by peroxides or oxygen as well as by light.[20] Kharasch assumes that bromine atoms are formed from hydrogen bromide by the action of peroxides or oxygen just as by the action of light and cause such effects. The effect of peroxides and oxygen on the addition of hydrogen bromide to ethenoid compounds was also explained on the assumption of bromine atoms.[18] Thus, the mechanism of the addition of hydrogen bromide to vinyl bromide, which was originally represented by electronic formulæ, may be put into ordinary formulæ as

(10) Y. Urushibara and M. Takebayashi, this Bulletin, **13** (1938), 331, 404, 574.
(11) *Idem, ibid.*, **11** (1936), 754.
(12) *Idem, ibid.*, **13** (1938), 400.
(13) *Idem, ibid.*, **13** (1938), 404.
(14) *Idem, ibid.*, **12** (1937), 51.
(15) M. S. Kharasch, J. V. Mansfield, and F. R. Mayo, *J. Am. Chem. Soc.*, **59** (1937), 1155.
(16) Y. Urushibara and O. S mamura, this Bulletin, **12** 1937), 507.
(17) *Idem, ibid.*, **13** (1938), 566.
(18) M. S. Kharasch, H. Engelmann, and F. R. Mayo, *J. Org. Chem.*, **2** (1937), 288.
(19) A. Berthoud and Ch. Urech, *J. Chim. Phys.*, **27** (1930), 291.
(20) M. S. Kharasch, E. Sternfeld, and F. R. Mayo, *J. Am. Chem. Soc.*, **59** (1937), 1655.

follows:

$$BrCH{=}CH_2 + HBr \rightarrow Br_2CH{-}CH_3 \quad \text{(normal reaction)}$$

$$HBr + O_2 \text{ (or peroxides)} \xrightarrow{CH_2{=}CHBr} HO_2 + Br$$

$$BrCH{=}CH_2 + Br \rightarrow BrCH{-}CH_2Br$$

$$BrCH{-}CH_2Br + HBr \rightarrow BrCH_2{-}CH_2Br + Br\,.$$

The essential features of these representations are that in the normal reaction the bromide ion is directed toward the carbon atom with the lowest electron density to yield 1,1-dibromoethane, and that in the abnormal reaction the bromine atom is directed toward the carbon atom with the greater electron density to yield a 1,2-dibromoethyl free redical. This free radical then reacts with hydrogen bromide to yield 1,2-dibromoethane and another bromine atom, which is responsible for the propagation of the chain reaction. According to this mechanism the function of peroxides or oxygen is to produce bromine atoms acting as chain carriers.

Hey and Waters[21] also suggested that the addition process of the abnormal reaction is one requiring the transient production of neutral atoms of hydrogen and bromine from hydrogen bromide.

Winstein and Lucas,[22] to explain the directive influence of oxygen in the abnormal additions of hydrogen bromide to the double bonds, assumed the formation of an oxygen complex from the unsaturated molecule prior to the addition of hydrogen bromide. It will be, however, soon self-evident that this theory cannot explain the experimental facts.

Urushibara and Takebayashi[14][6] also considered previously the mechanisms of the effects of oxygen and reduced nickel on the addition of hydrogen bromide to allyl bromide. The simplest explanation of the oxygen effect might be that the two reactions, one giving 1,2-dibromopropane and the other 1,3-dibromopropane, were simultaneous reactions proceeding without interfering with each other but with respective velocities determined by the concentrations of the reactants, oxygen accelerating the latter reaction only but being indifferent to the former. Such a simple explanation encounters at once serious difficulties. In the absence of oxygen 95% of the product is 1,2-dibromopropane. In the presence of oxygen 95% is 1,3-dibromopropane, while the total yield is not more than threefold in three days reaction. Assume that the two reactions were simultaneous reactions of the second order, then the following relations would exist:

$$x = y+z\,,$$

$$\frac{dy}{dt} = k_1(a-x)(b-x)\,,$$

$$\frac{dz}{dt} = k_2(a-x)(b-x)\,,$$

(21) D. H. Hey and W. A. Waters, *Chem. Rev.*, **21** (1937), 202.
(22) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60** (1938), 836.

$$\frac{dx}{dt} = (k_1+k_2)(a-x)(b-x) \qquad (1),$$

$$\frac{y}{z} = \frac{k_1}{k_2} \qquad (2),$$

where a and b represent the initial amounts of allyl bromide and hydrogen bromide respectively, x the amount of allyl bromide which reacts in time t, y and z the amounts of 1,2- and 1,3-dibromopropanes formed in time t respectively, and k_1 and k_2 constants. The above simple explanation requires only an increase of k_2 to k_2' in the presence of oxygen. The ratio $(k_1 + k_2')/(k_1 + k_2)$ can be evaluated from (1) and from (2) independently: Inserting the values obtained in the experiments,[5] values 3.3–5.4 are obtained from the relation (1) of the total reaction velocity while 19–22 from the relation (2) of the composition of the reaction product.

In the cases of vinyl bromide[23] and vinyl chloride[24] the reversal of the direction of addition by oxygen is more conspicuous: In the absence of oxygen the product is 100% ethylidene dihalide while in the presence of oxygen 100% ethylene dihalide. The fact that the normal reaction does not occur at all in the presence of oxygen cannot be explained on the assumption of the mere acceleration of the abnormal reaction by oxygen. Another difficulty is that the total yield of the products from allyl bromide and hydrogen bromide increases with the amount of oxygen admitted even after the proportion of 1,3-dibromopropane has reached the constant maximal value (95%); that is to say, the absolute yield of 1,2-dibromopropane decreases rapidly as the amount of oxygen increases until the latter reaches a certain amount and thence increases in the same rate as that of 1,3-dibromopropane.[5]

Smith[25] has briefly reported that the normal reaction of undecenoic acid and hydrogen bromide with thorough elimination of oxygen proceeded with a rate less than one-fiftieth of the speed of the abnormal reaction. It suffices, however, to point out that allyl bromide and hydrogen bromide give a product containing 95% 1,2-dibromopropane in a certain yield under a set of conditions and another product containing 95% 1,3-dibromopropane in a yield not more than three times as much under another set of conditions which differs from the former only in that a certain amount of oxygen is admitted. In the experiments by Urushibara and Takebayashi[10] on the addition of hydrogen bromide to undecenoic acid in toluene solution quantitative yields were always obtained regardless of the conditions and of the compositions of the products.

In the presence of reduced nickel which has never been in contact with air, allyl bromide and hydrogen bromide give a product containing 95% 1,3-dibromopropane in a total yield only twice as much as that obtained in the absence of the catalyst.[14] Reduced nickel is a heterogeneous catalyst, yet the normal reaction giving 1,2-dibromopropane is

(23) M. S. Kharasch, M. C. McNab, and F. R. Mayo, *J. Am. Chem. Soc.*, **55** (1933), 2521.
(24) M. S. Kharasch and C. W. Hannum, *ibid.*, **56** (1934), 712.
(25) J. C. Smith, *Chemistry and Industry*, **57** (1938), 464.

inhibited throughout the reacting system, the bulk of which is not in contact with the catalyst.

Thus Urushibara and Takebayashi[6] was led to assume that in the presence of a sufficient amount of oxygen (or reduced nickel) the catalyzed addition only takes place, and that the catalyzed addition yields a product consisting of 95% 1,3-dibromopropane and 5% 1,2-dibromopropane. The amount of oxygen just sufficient for producing the maximal proportion (95%) of 1,3-dibromopropane is 1.5 c.c. (n.p.t.) for 24 g. allyl bromide and 20 g. hydrogen bromide in a reaction vessel of 140 c.c. capacity.[5] Even if the whole oxygen were dissolved in the liquid, only one molecule of oxygen would be available for 3,000 molecules of allyl bromide. From a very fascinating speculation that the actions of oxygen and reduced nickel might be connected with their magnetic properties, it was assumed that each molecule of oxygen would exert some physical influence over at least 3,000 molecules of allyl bromide.

If the direction of addition of hydrogen bormide were decided according to the polarity of the allyl bromide molecule, how could one molecule of oxygen reverse totally the polarity of so many molecules of allyl bromide? Although it has been made probable that the substance to be influenced by oxygen and reduced nickel is hydrogen bromide,[16] it is non the less difficult to understand how one molecule of oxygen could exert a physical influence on thousands of molecules of hydrogen bromide. Thus the assumption of a chain mechanism seems necessary as in the case of a photochemical reaction with a great quantum yield.

Although Kharasch's theory of the chain reaction involving bromine atoms has obtained nearly no experimental evidence except an analogy with the photochemical reactions, no objection can be raised from the experimental results obtained by Urushibara and co-workers. On the contrary, the formation of stilbene dibromide in the experiment of isomerization of isostilbene by hydrogen bromide and oxygen in benzene solution seemed to favour Kharasch's theory.[17] Considering the very close resemblance of the effects of oxygen and reduced nickel, it may be presumed that the essential parts of the mechanisms of their actions are the same; yet there have been obtained no bases nor analogies to postulate the formation of bromine afoms from hydrogen bromide and reduced nickel. Thus the present authors have been led to carry out the experiments described below and elsewhere to discuss on Kharasch's theory on the one hand and to know the mechanism of the action of reduced nickel on the other, and, as for the mechanism of the oxygen effect, not only Kharasch's theory has been substantiated in principle but also a more comprehensive treatment of the matter has been made on the basis of the experimental results.

Action of Hydrogen Bromide and Oxygen on Catechol. As it seemed that the antioxidants would afford a clue to elucidation of the mechanism of the oxygen effect, the behaviour of catechol, the most effective of the antioxidants used in this laboratory, towards oxygen and hydrogen bromide was examined.

To a solution of 0.5 g. of catechol in 140 g. of carbon tetrachloride (catechol remained partly undissolved) a mixture of hydrogen bromide

and oxygen was passed for two hours in the dark at room temperature. No sign of change was noticeable and from the reaction mixture which had stood overnight the whole amount of catechol was recovered unchanged. Thus it was demonstrated that hydrogen bromide and oxygen do not unconditionally (or even in the presence of catechol) produce atoms or molecules of bromine. As it was then anticipated that the presence of an unsaturated compound might be essential for the formation of bromine atoms from hydrogen bromide and oxygen, the following experiments were carried out.

Action of Hydrogen Bromide and Oxygen on Allyl Bromide. Hydrogen bromide and oxygen do not react at room temperature as shown by the above experiment. Further it was previously observed that no peroxide was produced from allyl bromide and oxygen in the dark, but diffuse light caused the formation of a peroxide in a few days.[4]

Commercial allyl bromide was purified by washing with water and distilling in the dark, and a portion boiling at a constant temperature was used preferably immediately after distillation. Hydrogen bromide and oxygen were dried separately by passing over phosphorus pentoxide, mixed in a T-tube, and introduced into allyl bromide cooled with ice water in the dark (without cooling much heat was evolved causing the evaporation of allyl bromide). Changes were occasionally observed in dim light from an incandescent lamp. Much complicated reactions were perceived to occur during the passage of the gas mixture. There was no change in the beginning, but by and by the allyl bromide became turbid until drops of a liquid were distinctly observed on its surface. After a while it was noticed that the liquid became faintly yellow for a moment on shaking, indicating the liberation of bromine. The temporary coloration appearing on shaking grew deeper gradually but disappeared at once. Finally the coloration due to bromine persisted, but the liberation of bromine was not carried on beyond a certain extent on continuing the passage of the gas mixture.

The weight of the reaction products corresponded nearly to the amount expected from the addition of hydrogen bromide to allyl bromide, if it was taken into account that part of allyl bromide might have been carried away with the gas mixture. The liquid which separated on the surface was recognized as water. The colourless reaction mixture set free iodine from aqueous potassium iodide acidified with hydrochloric acid, showing that a peroxide had been formed in the reaction. The peroxide, however, is fairly stable and does not decompose easily, and the liberation of iodine from the iodide solution was not completed even when heat was applied. When the reaction mixture was shaken with water, the peroxide was found to shift partly to the aqueous layer as was shown by the liberation of iodine from the iodide solution. The liberation of iodine, however, was very slowly brought to completion even in the aqueous solution. Owing to such stability of the peroxide it was difficult to determine exactly its amount by titrating liberated iodine with a standard thiosulphate solution, but it was roughly estimated that the amount of the peroxide corresponded to 0.1 to 0.2 g. atom of iodine per 1 mole of allyl bromide used. The formation of the peroxide was detected

even after a few minutes' action of the gas mixture.

When the reaction mixture was washed with water, dried, and distilled under the atmospheric pressure, vigorous decomposition of the peroxide set in and hydrogen bromide was evolved. No fractions corresponding to allyl bromide and 1,2-dibromopropane were obtained and the temperature of the vapour rose abruptly, the greater part distilling near the boiling point (165°) of 1,3-dibromopropane. A fraction distilling above 200° was obtained in an amount corresponding to less than one-tenth of the whole products and a small amount of a carbonized matter remained in the flask. Thus 1,3-dibromopropane was found to form the greater part of the whole products.

As already mentioned, there occurs no change between allyl bromide and oxygen on the one hand and between hydrogen bromide and oxygen on the other. When hydrogen bromide was passed into allyl bromide in the same apparatus as used in the above experiment 1,3-dibromopropane was formed almost quantitatively (air being not excluded, the abnormal reaction took place), but neither water nor peroxide was produced. It is only when all three of allyl bromide, hydrogen bromide and oxygen are present that the reactions as described above take place.

Water seems to have been yielded from hydrogen peroxide which may have been primarily formed. The reasons are as follows: In general the first stage of the oxidation by molecular oxygen is the formation of peroxides. On passing hydrogen bromide and oxygen into allyl bromide a certain amount of bromine liberated remained unconsumed, thus suggesting that the oxidation of hydrogen bromide to bromine occurred to some extent even after the whole allyl bromide had reacted. Inasmuch as the organic peroxide is stable in the presence of much hydrogen bromide as mentioned above it could not be the oxidizing agent. The direct oxidation of hydrogen bromide by oxygen having been ruled out, the only remaining alternative is that the formation of water and bromine is caused by the action of hydrogen peroxide primarily formed on hydrogen bromide.

The bromine thus formed must enter into reaction with allyl bromide, yielding 1,2,3-tribromopropane (b.p. 219–221°), which may have been contained in the fraction boiling above 200°. In a separate experiment 1,2,3-tribromopropane was prepared by adding bromine to allyl bromide and was found not to liberate iodine from aqueous potassium iodide acidified with hydrochloric acid.

It has been established by Bockemüller and Pfeuffer[26] that the simultaneous action of bromine and oxygen on allyl bromide gives a peroxide $(BrCH_2)_2CH\text{-}O\text{-}O\text{-}CH(CH_2Br)_2$ besides the tribromopropane. In the present case a part of the peroxide may have been resulted from allyl bromide, oxygen and the secondarily formed bromine by the same process as in the German investigators'; but that this is of subordinate importance is obvious on the following ground. Though the experiments by Bockemüller and Pfeuffer were performed under the conditions most favourable to the action of oxygen, the molar ratio of the oxygen consumed to the bromine which reacted was found as 1:6.5 (25°), corre-

(26) W. Bockemüller and L. Pfeuffer, *Ann.*, **537** (1939), 178

sponding to the formation of less than one mole of the peroxide while five moles of the tribromopropane were produced. It was manifest in the present experiments that five times as much tribromopropane as the peroxide (as much as 0.4 mole of the tribromopropane for one mole of allyl bromide) and the corresponding amount of water (0.5 mole from one mole of allyl bromide) were not formed. In an experiment with 0.4 mole of allyl bromide the amount of water formed was estimated with the eye to amount only to a few tenths of 1 c.c.; and less than ten per cent of the whole products distilled near the boiling point of 1,2,3-tribromopropane. Hence, it must be concluded that the peroxide obtained in the present case was produced at least for the most part by the direct action of allyl bromide, oxygen and hydrogen bromide.

Action of Hydrogen Bromide and Oxygen on Stilbene. It has already been mentioned that in the isomerization of isostilbene by hydrogen bromide and oxygen in benzene solution a small amount of stilbene dibromide was formed.[17] To examine the action of hydrogen bromide and oxygen upon stilbene the gas mixture was passed into a benzene solution (50 c.c.) of stilbene (0.218 g.) under the same conditions as in the experiments with allyl bromide. After about fifteen minutes' passage of the gas mixture it was noticed that the solution had become yellow with bromine, and the coloration did neither fade on shaking nor become deeper on continuing the passage of the gas mixture. The gas was passed further for five minutes. When a sample from the reaction mixture was added to aqueous potassium iodide iodine was liberated and the benzene layer became violet. When the reaction mixture was evaporated in vacuum at room temperature there remained fine crystals embedded in an orange-coloured oil having an aromatic odour. The whole products weighed 0.433 g., while if all the stilbene used was to be converted into the dibromide it should give 0.412 g. A small volume of benzene was added to the mass and the crystalline substance was collected on a sheet of filter paper. It melted at 238° with decomposition and was identified as stilbene dibromide by the melting point of a mixture with an authentic specimen. The benzene extract contained a small amount of a peroxide as indicated by the test with ferrous ammonium sulphate and ammonium thiocyanate. The nature of the oily product was not further pursued.

As a control experiment the gas mixture was passed into pure benzene (50 c.c.) for 25 minutes, but neither any coloration of the liquid nor the liberation of iodine on shaking the benzene with the iodide solution was observed.

The Mechanisms of the Reactions of Hydrogen Bromide, Oxygen and the Ethenoid Compounds as well as the Mechanism of the Abnormal Addition in the Presence of Oxygen. On the basis of the experimental results and the interpretation of them described above, the reactions in question seem to be represented by the schemes as shown below for the case of allyl bromide. The oxidation of hydrogen bromide by oxygen takes place with allyl bromide as a necessary acceptor of bromine atoms, giving rise to hydrogen peroxide and a dibromoisopropyl radical:

$$2CH_2{=}CH{-}CH_2Br + 2HBr + O_2 \rightarrow 2BrCH_2{-}\underset{|}{CH}{-}CH_2Br + H_2O_2 .$$

Here the diradical nature of oxygen comes into play, and the production of hydrogen peroxide may probably be preceded by the intermediate formation of a radical HO_2. Thus the above process may have to be further resolved into steps. An expression such as $2HBr + O_2 \rightarrow 2Br + H_2O_2$, however, should be avoided, because it is to be emphasized that the oxidation of hydrogen bromide by oxygen is only possible in the presence of an ethenoid compound.

Then the organic peroxide forms itself with all probability from the dibromoisopropyl radical and oxygen, and thus may be identical with that formed in the reaction of Bockemüller and Pfeuffer:

$$2BrCH_2-\underset{|}{CH}-CH_2Br + O_2 \rightarrow (BrCH_2)_2CH-O-O-CH(CH_2Br)_2 .$$

Even in the presence of much oxygen the greater part, and in the presence of a small amount of oxygen almost all, of the dibromoisopropyl radical starts the following chain reaction:

$$BrCH_2-\underset{|}{CH}-CH_2Br + HBr \rightarrow BrCH_2-CH_2-CH_2Br + Br$$

$$CH_2=CH-CH_2Br + Br \rightarrow BrCH_2-\underset{|}{CH}-CH_2Br .$$

The abnormal additions of hydrogen bromide to ethenoid compounds can be considered to proceed by such chain processes.

The hydrogen peroxide oxidizes hydrogen bromide to produce bromine and water:

$$H_2O_2 + 2HBr \rightarrow 2H_2O + Br_2 ,$$

and the bromine set free adds probably for the most part to allyl bromide to yield 1,2,3-tribromopropane:

$$CH_2=CH-CH_2Br + Br_2 \rightarrow BrCH_2-CHBr-CH_2Br .$$

It may also be possible that the tribromopropane results from the addition of a second bromine atom to the dibromoisopropyl radical.

Inasmuch as the radicals and some of the compounds taking part in the above mechanism are to be considered as very reactive, there may be many other possibilities of reactions among them. For the sake of simplicity, however, only those processes that are necesary to explain what has been observed are considered. Minor particulars cannot be decided from the results so far obtained.

In the case of stilbene, the reaction seems to follow a course like the above in the main, but stilbene dibromide is the main product in this case and seems to be formed for the most part by the addition of two atoms of bromine in two steps.

The inhibiting action of the antioxidants on the abnormal addition reactions is considered to consist in capturing bromine atoms, thus interrupting the propagation of chains.

That the molecular bromine does not accelerate the abnormal addition has been shown by Smith.[27] In the addition of hydrogen bromide

(27) J. C. Smith, *Chemistry and Industry*, **57** (1938), 465.

to undecenoic acid in dilute benzene solution, the addition of much bromine caused the abnormal addition, but the necessary amount was very large compared with that of oxygen which was efficient enough in traces. In a concentrated solution hydrogen bromide added normally although bromine was consumed.

Thus not only Kharasch's hypothesis has been experimentally substantiated and it has been established that hydrogen bromide and oxygen give rise to bromine atoms in the presence of ethenoid compounds, but also the fate of hydrogen atoms and the reactions to proceed in the presence of much oxygen have been made clear.

The Mechanism of the Normal Addition. Since the double bond at the end of a chain, and especially the terminal unsaturated carbon atom, are associated with the least steric hindrance, it can be anticipated from a steric point of view that addition will take place at this carbon atom with the greatest ease. Thus, if hydrogen bromide adds by atoms, the atom adding first to the double bond, whether it may be the bromine atom or the hydrogen atom, will prefer the terminal position. No contradiction is tenable from the consideration of the electron density, because the atom, whether bromine or hydrogen, will be directed toward the terminal carbon atom with the greater electron density and it is hardly possible that the electron density should be affected by oxygen. If the initiative in addition, hence the terminal position, is taken exclusively by the bromine atom or by the hydrogen atom, then the product will contain a predominating proportion of either of the two isomerides. In the addition of hydrogen bromide to ethenoid compounds with terminal double bonds, e.g. allyl bromide and vinyl bromide, the products obtained under extreme conditions consist mainly or solely of either of the two possible isomerides. It must be noted here that in the above-mentioned examples oxygen exactly reverses the proportion of the two isomerides. An inspection of the constitutions of the main or sole products indicates at once that the initiative in addition is taken by the hydrogen atom in the normal reaction and by the bromine atom in the abnormal reaction. The abnormal reaction taking place in the presence of oxygen has just been explained on the basis of a chain mechanism involving the bromine atom and the radical formed by the addition of the bromine atom to the terminal carbon atom of the unsaturated molecule. The fact that the normal reaction is inhibited totally as the abnormal one becomes active, is well understood on the assumption that the normal reaction is also a chain reaction (see below). Thus the normal reaction may be represented by the following scheme:

$$CH_2{=}CH{-}CH_2Br + H \rightarrow CH_3{-}\underset{|}{CH}{-}CH_2Br$$

$$CH_3{-}\underset{|}{CH}{-}CH_2Br + HBr \rightarrow CH_3{-}CHBr{-}CH_2Br + H\,.$$

Even in the presence of a sufficient amount of oxygen about 5% of the product from allyl bromide and hydrogen bromide is 1,2-dibromopropane, while in the absence of oxygen 1,3-dibromopropane is formed in a proportion of about 5%. Thus it can be assumed that about one-twentieth of the atoms, either bromine or hydrogen, taking the initiative in

addition add to the carbon atoms adjacent to the terminal carbon atoms rather than that the atoms adding first are all directed to the terminal carbon atoms and consist of 95% of one and 5% of the other, because in the cases of vinyl halides it must be concluded that all the atoms taking the initiative in addition are either bromine atoms or hydrogen atoms and add exclusively to the terminal carbon atoms, indicating that the compositions of the products obtained under extreme conditions depend entirely on the nature of the unsaturated molecules.

The accelerating effect of platinum black on the normal reaction may be attributed to the activation of the hydrogen atom of hydrogen bromide which takes the initiative in addition. The following facts support this idea: (1) While reduced nickel does not act as a hydrogenating catalyst at ordinary temperature, platinum black can activate hydrogen at ordinary temperature and pressure. (2) If hydrogen bromide is added to allyl bromide in the presence of both platinum black and oxygen, the composition of the product is intermediate and in this case bromine is liberated and remains free in spite of the presence of allyl bromide unchanged.[4] This may be interpreted as that the hydrogen atom activated by platinum black combines partly with oxygen while the unpaired bromine atom cannot add even to the unsaturated allyl bromide and is thrown off temporarily as a bromine molecule.

Since it seems that the normal reaction, or strictly speaking the reaction giving the same product as the normal reaction, accelerated by platinum black and the abnormal reaction caused by oxygen proceed side by side, the addition initiated by the hydrogen atom activated by platinum black is probably concluded by the combination of the remaining bromine atom to form 1,2-dibromopropane without commencing the chain reaction as shown above (further see below).

The Cancelling of the Normal and the Abnormal Chains. If the normal and the abnormal chains are brought into co-existence, the bromoisopropyl radical and the hydrogen atom of the former may combine with the bromine atom of the latter on the one hand, and, on the other, the dibromoisopropyl radical and the bromine atom of the abnormal chain may combine with the hydrogen atom of the normal chain. Thus cancelling of the two kinds of chains may occur and either kind remaining after this process will be propagated freely. After all the chains propagating in the system have become abnormal ones, the increase of the chains by increasing the amount of oxygen will cause only the increase of the reaction velocity without affecting the composition of the product. The experimental results are in perfect accordance with this.[5]

According to the above idea, the abnormal and the normal reactions cannot proceed side by side both in considerable intensities during a long time. Thus the fact that products of intermediate compositions are obtained under intermediate conditions needs an explanation. This affords, however, no indication that the two reactions should proceed side by side in a ratio that might be revealed by the compositions of the products. On the contrary, a simple calculation from the data obtained previously[5] makes it quite clear that under such conditions the normal chains pre-

dominate in the first stage of the reaction but are gradually supplanted by the abnormal chains.

Amount of oxygen admitted (c.c.)	Total yield (%)			1,3-Dibromopropane (%) in the product formed in		
	3 days	5 days	Diff.	3 days	5 days	Last 2 days in 5 day reaction
0*	14	24	10	4	12	23
0.5	21	37	16	38	60	89

* A minute quantity of oxygen may have possibly been present, because the evacuation of air was effected with a rotary pump.

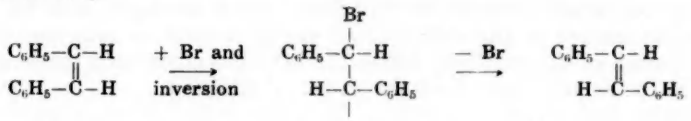
The accompanying table shows that the normal reaction is gradually supplanted by the abnormal reaction with the lapse of time. Such a phenomenon, which may be represented by the term "induction period," must occur also within 3 days, and it goes without saying that the more oxygen is present the quicker the abnormal reaction takes the place of the normal one. Thus the intermediate composition represents only the sum of products formed in the course of such rise and fall of the two reactions, and not the proportion with which the two reactions proceed all the time.

It is not impossible that oxygen may inhibit the normal reaction by catching the hydrogen atom carrying the normal chain; however, as the normal reaction can be eliminated by a very small amount of oxygen such a mechanism may not be responsible for the formation of water (or hydrogen peroxide) in the reaction of allyl bromide, hydrogen bromide and oxygen.

The Mechanism of the Cis-trans Isomerization by Hydrogen Bromide and Oxygen. It has already been suggested that the isomerization of isostilbene to stilbene by hydrogen bromide and oxygen may be closely related with the addition of hydrogen bromide to ethenoid compounds in the presence of oxygen. Thus it may reasonably be assumed that the first stage of the isomerization is the same as that of the addition, namely, the addition of the bromine atom formed from hydrogen bromide and oxygen to produce a bromo radical. Here the second stage of addition, namely, the formation of the completed addition product and another bromine atom, does not occur owing to the small concentration of hydrogen bromide and especially to the nature of the unsaturated linkage, but the bromine atom which has entered the unsaturated molecule goes out and moves to another molecule of the unsaturated compound. Thus the mechanism is quite analogous to that of the isomerization by bromine and light. However, the addition of a bromine atom to the double bond, free rotation about the single bond thus formed and elimination of the bromine atom, as postulated by Berthoud[19][28], do not explain the inversion of the geometrical isomerides. The addition (or the elimination)

(28) Compare further D. H. Hey and W. A. Waters, *Chem. Rev.*, **21** (1937), 169 and W. A. Waters, "Physical Aspects of Organic Chemistry," 139, London (1937).

of the bromine atom should be accompanied by an inversion of either of the unsaturated carbon atoms.[29] Then the isomerization of isostilbene by hydrogen bromide and oxygen may be represented as a chain reaction shown below:



The inhibiting action of antioxidants on the cis-trans isomerization by hydrogen bromide and oxygen can be attributed also to the break of the chains due to the capture of bromine atoms by them.

If much hydrogen bromide and oxygen be present, the bromo radical takes up another bromine atom to form stilbene dibromide rather than hydrogen atom from hydrogen bromide.

Cases where the Effect of Oxygen is Undetectable. It is beside the question of the present paper whether or not oxygen will affect the additions of hydrogen bromide proceeding by other mechanisms, e.g., ionic addition. The effect of oxygen, however, may be undetectable in certain cases of atomic additions by the chain mechanism.

Let the two unsaturated carbon atoms be designated as α and β. If the α carbon atom is terminal, any atom adding first will prefer it. In the case of allyl bromide 95% of the atoms adding first are directed to the α carbon atoms, while in cases of vinyl halides all the atoms adding first combine with the α carbon atoms. Here it may be pointed out again that, whether the atoms adding first are bromine or hydrogen, they are distributed between the α and β positions in the same proportion.

If the double bond is not situated at the end of a chain and the α and β carbon atoms are alike in their properties, the atoms adding first may tend to be distributed equally between the α and β carbon atoms. In such a case the product may be near to a 50%:50% mixture of two isomerides, and irrespective of the kind of the atoms adding first the result of addition may be the same if seen from the composition of the product, and, therefore, the effect of oxygen may be difficult to detect.

Thus, Smith and co-workers[30] observed that the addition of hydrogen bromide to isoundecenoic acid or to the corresponding alcohol gives a mixture containing equal amounts of two isomerides either in the presence or in the absence of oxygen. Further Kharasch and co-workers[31] added hydrogen bromide to *cis*- and *trans*-pentene-(2) and obtained equal amounts of 2-bromopentane and 3-bromopentane regardless of the conditions of addition and of the spatial configuration of pentene-(2).

The distribution of the bromine atoms adding first between the α and β carbon atoms may not always be equal to that of the hydrogen

(29) Compare R. L. Shriner, R. Adams, and C. S. Marvel, "Gilman's Organic Chemistry," Vol. I, 378, New York (1938).

(30) P. L. Harris and J. C. Smith, *J. Chem. Soc.*, **1935**, 1108; E. P. Abraham, E. L. R. Mowat, and J. C. Smith, *ibid.*, **1937**, 948.

(31) M. S. Kharasch, C Walling, and F. R. Mayo, *J. Am. Chem. Soc.*, **61** (1939), 1559.

atoms, and thus the normal and the abnormal reactions may not always give products with reciprocal compositions. In the special case where the distribution of the bromine atoms is a reciprocal of that of the hydrogen atoms, the compositions of the products will be equal in spite of the quite different modes of reactions. Such examples will be found in case the nature of the substituents exerts a decisive influence on the determination of the positions which the bromine atoms and the hydrogen atoms can take irrespective of the order of addition.

Conclusion and Summary. When hydrogen bromide acts on the ethenoid linkage in the presence of oxygen, the first change to be characterized is the formation of a bromo radical from the unsaturated molecule and the bromine atom formed from hydrogen bromide and oxygen. In the formation of the bromo radical, if the double bond is situated at the end of a chain, the bromine atom takes preferably the terminal position, and, if an asymmetric carbon atom is produced by the addition of the bromine atom, inversion is accompanied. In the second stage of the reaction the radical, according as its nature and the conditions, either takes up hydrogen atom from hydrogen bromide to form a completed addition product and another bromine atom or splits off the bromine atom to regenerate the double bond. In either case the cycle of the changes is propagated by a chain mechanism. The action of oxygen, therefore, resembles that of light quantum in a photochemical reaction proceeding with a great quantum yield.

The theory advanced in this paper is based on the experiments on the action of hydrogen bromide and oxygen on certain ethenoid compounds.

The effect of reduced nickel will be discussed in a separate paper on the basis of a quite similar mechanism.

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